

Properties of star-branched and linear chains in confined space: a computer simulation study

Piotr Romiszowski* and Andrzej Sikorski

Department of Chemistry, University of Warsaw, 02-093 Warszawa, Poland
E-mail: prom@chem.uw.edu.pl

We studied the properties of simple models of linear and star-branched polymer chains confined in a slit. The polymer chains were built of united atoms and were restricted to a simple cubic lattice. Two macromolecular architectures of the chain: linear and star-branched with three branches (of equal length) were studied. The excluded volume was the only potential introduced into the model and thus, the system was athermal. The chains were put between two parallel and impenetrable surfaces. Monte Carlo simulations with a sampling algorithm based on chain's local changes of conformation were carried out. The differences and similarities in the global size and the structure and of linear and star-branched chains were shown and discussed.

KEY WORDS: branched polymers, confined polymer, lattice models, linear polymers, Monte Carlo method

1. Introduction

The presence of the confinement between impenetrable surfaces changes dramatically most of the properties of polymers when compared with the free (unconfined) chains in solution. This problem is important due to its practical applications like lubrication, polymer films, and colloidal stabilization. It is also interesting from the theoretical point of view, because of substantial restriction of the chain's conformational space [1, 2]. The experiments showed that the force acting on the confined polymer chains was repulsive and long-ranged [2]. Recently, such confined systems were frequently studied by means theoretical considerations and computer simulations [3–10]. Differences in the static and dynamic properties as well the phase behavior of chains in the bulk and in the confinement were shown. However, most of these studies concerned linear homopolymers and block copolymers chains only. Simple scaling theory of confined star-branched chains was done by Halperin and Alexander [5] while Monte

*Corresponding author.

Carlo simulations of simple models of confined star polymers were carried out by Romiszowski and Sikorski [9] and Sikorski and Romiszowski [10].

The purpose of this study was to investigate the influence of the confinement and the chain topology on some properties of polymer chains. The open question is whether or not the internal macromolecular architecture has significant influence on the properties of confined chains. Since the performing of a full atom simulation of the system is impossible one has to introduce some simplification. Hence, we developed and studied simplified polymer models. In this model we used a united atom representation and the lattice approximation. Within the frame of this model we studied single polymer chains what corresponded to infinite diluted solution. The chains were put into a slit formed by a pair of two impenetrable surfaces. Two different types of polymer chains having different macromolecular architecture were studied: linear chains and regular star-branched chains.

2. The model

The model polymers were extremely simplified in order to make the calculations possible for larger systems and for longer time scales. All the atomic details were skipped and the chains consisted of united atoms called polymer segments. The locations and orientations of these segments were limited to vertices of a simple cubic lattice. The polymer segments formed two different kinds of chains: linear chains and the star-branched chains. The latter polymer consisted of three linear chains starting from a common origin called the branching point. The chains were athermal and the only intra-chain potential of interactions was the excluded volume (the forbidding of the double occupancy of lattice sites). We studied diluted solution of confined polymers and therefore single model chains consisted of N identical segments were put between two impenetrable parallel surfaces in the distance d . The surfaces were perpendicular to the axis z and in the two remaining directions of space x and y periodic boundary conditions were imposed [9]. Schematic representation of the both model chains in the slit formed by the confining surfaces are presented in figure 1. It was previously shown that such simple models are sufficient for studying the properties of chain on the scale larger than a single segment.

The model polymer systems were studied by means of dynamic Monte Carlo method. In the simulation, we used a Verdier–Stockmayer type algorithm in which the conformation of a polymer chain was locally modified. The following set of micromodifications was employed for this purpose: 2-bond move, 3-bond move, 3-bond crankshaft move, 1-bond, and 2-bond chain's ends moves. The star-branched chains were also the subjects of the branching point collective motion what enabled the whole macromolecule to move freely within the space confined by the two walls and with no limits in xy plane (figure 2). Each

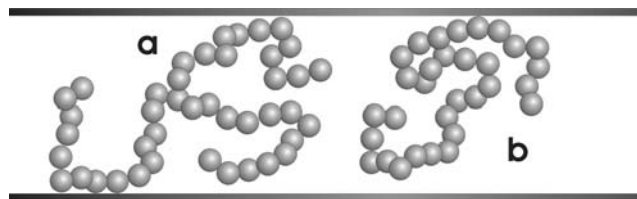


Figure 1. Scheme of the chains confined between the two parallel impenetrable surfaces located at distance d apart: star-branched (a) and linear (b).

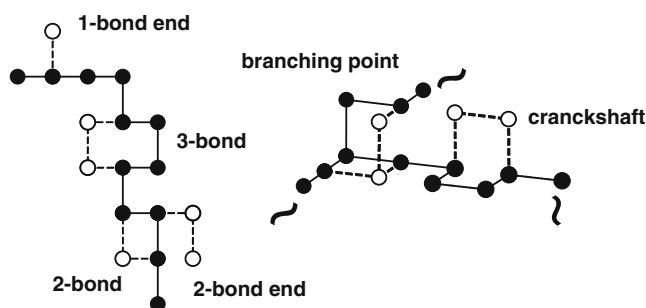


Figure 2. Scheme of the chain's micromodifications.

of the chain segments was the subject of one attempt of all micromodifications, what defined the time unit (the Monte Carlo step). The position of the fragment of the chain that was modified was picked at random. The acceptance of the micromodification was done due to the excluded volume and topological constrains [11].

The simulations were performed according to the following protocol. An initial conformation of a chain was built randomly and the system was equilibrated, i.e. 10^5 – 10^6 Monte Carlo steps. Then, a production run was performed with 10^7 – 10^8 time units. For each system under consideration (N , d , architecture) 20–30 Monte Carlo simulation runs were carried out starting for different initial conformation. The resulting trajectories were then analyzed and the properties of the molecules were determined. The standard deviations of the results obtained from the trajectories started from different initial conformations did not exceed 3%.

3. Results and discussion

The Monte Carlo simulations were performed for star-branched and linear chains that contained the same number of segments $N = 50, 100, 200, 800,$ and 1200 in order to make the results comparable for both types of chains. We studied properties of our model chains for distances between the two parallel

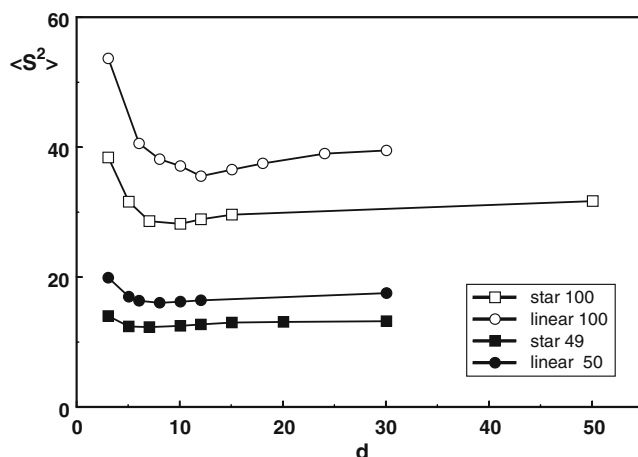


Figure 3. The mean-squared radius of gyration $\langle S^2 \rangle$ as a function of the distance between the surfaces. The chain architectures and the chain lengths are given in the inset.

impenetrable surfaces between $d = 3$ (the smallest possible distance at which the Monte Carlo algorithm can sample the conformational space) and $d = 180$ (the longest chains are almost not squeezed by the confining surfaces).

We have studied the size of macromolecules, which was as usually described by the mean-squared radius of gyration $\langle S^2 \rangle$. The choice of this parameter was done due to the fact that it describes the size of the entire macromolecule what is essential for a study of the impact of the confinement. Figure 3 presents the dependence of this parameter on the confinement, i.e. on the distance between the surfaces d . One can observe that for both chain architectures the course of the plot is qualitatively the same. When the confinement becomes stronger (the distance d decreases) the size of chain diminishes. Further squeezing of the chain leads to the increase of its size, i.e. of the radius of gyration. This behavior can be explained by the fact that chains underwent the transition from three-dimensional to two-dimensional structure. The only difference between linear and star-branched chains was the lower values of $\langle S^2 \rangle$ for the first case and the minimum was shifted for star polymers toward larger distances between the surfaces.

In order to compare the effect of confinement on the chains of different length, we used reduced quantities. For this purpose the mean-squared radius of gyration of each chain was normalized dividing it by the values of $\langle S^2 \rangle_0$ which were determined for unconfined chains of the same length and architecture. In figure 4, we plotted the ratio $\langle S^2 \rangle / \langle S^2 \rangle_0$ against the normalized size of the slit, which was calculated as

$$d^* = \frac{d}{2\sqrt{\langle S^2 \rangle_0}}. \quad (1)$$

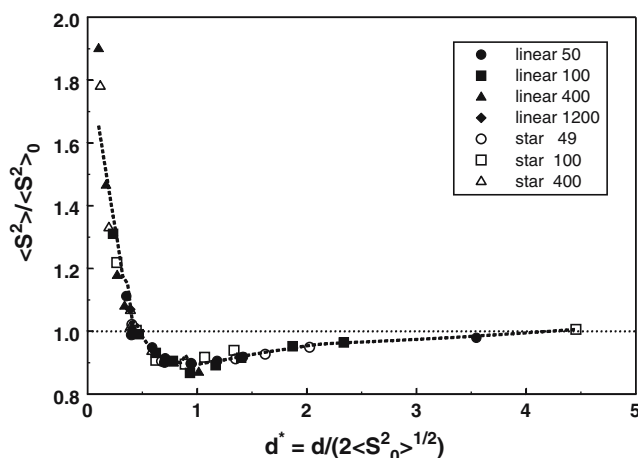


Figure 4. Plot of the reduced radius of gyration $\langle S^2 \rangle / \langle S^2 \rangle_0$ as a function of the reduced distance between the surfaces d^* for. The chain architectures and the chain lengths are given in the inset.

The choice of the parameter d^* was determined by the fact that $2 \langle S^2 \rangle_0^{1/2}$ corresponds to the diameter of ‘free’ (unconfined) chain. One can observe that the calculated values for all chain lengths and for both architectures are located along a common curve. The shape of this curve is similar to the curves presented in figure 3. It has one minimum in the vicinity of $d^* = 1$. The above behavior suggests the common behavior of all linear and star-branched chains under confinement. Similar dependencies were found for quite different polymer models as well as for a polymer melt [2].

The influence of the confinements on the local ordering in the chain was also studied. Figure 5 presents the mean-squared cosine of the angle φ formed between a polymer segment and the z -axis (the direction perpendicular to the surfaces). One can observe that there is no significant difference between ordering of polymer segments for all chain lengths and both architectures. The changes in the ordering of segments strongly depend on the z coordinate. The ordering parameter $\langle \cos^2 \varphi \rangle$ changes almost of order of magnitude when going from the vicinity of the confining surfaces towards the middle of the slit. It can be explained by the fact that near the surfaces polymer segments try to locate parallel to the walls and the perpendicular direction is discriminated. In the middle of the slit more perpendicular orientations can appear in spite of the fact that the segment density is the highest there [5].

The exposure of the confined chain and its parts on the surfaces can be described by the number of contacts between the chain segments and the walls. The frequencies of the contacts were determined for each bead of the chain separately. In order to make the results comparable for both architectures we introduced a specific bead numbering. For star-branched chains bead numbering went

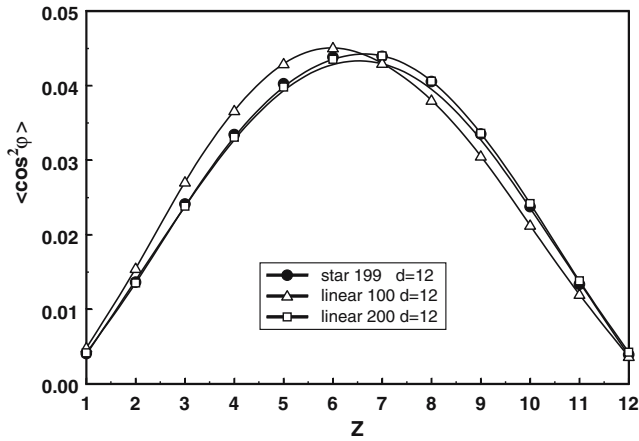


Figure 5. The ordering of polymer segments as a function of the distance from a wall z . The chain architectures and the chain lengths and the distances between the walls d are given in the inset.

from the branching point to an end of an arm. The linear chains were treated as the star with two branches of length $N/2$ and, therefore, the numbering went from the middle of the chain to an end of the chain. In order to compare the results for different chain length we normalized them in the spirit similar to the reduced size of chain discussed above. The reduced frequencies of polymer segment-surface contacts were defined as follows:

$$f_i^* = \frac{f_i \cdot n}{\sum_i f_i}, \quad (2)$$

where f_i is the number of contacts per one time unit. From figure 6 one can see that the normalized frequency data for all chain lengths and for different confinement form one common curve. However, curves for each of architectures are different. In the curve for star-branched molecules one can observe three different regimes: one on the vicinity of the branching point ($i/n < 0.1$), then the plateau region ($i/n = 0.1 \div 0.9$) and finally the end of chain region ($i/n > 0.9$). The curve for the linear chains consists only of a plateau and the end chain region ($i/n > 0.8$). This difference between the curves is caused by presence of the relatively high segment density in the vicinity of the branching point for the star-branched molecules. The presence of such dense core was predicted theoretically and confirmed by computer simulation studies concerning the case of 'free' (unconfined) chains [12].

One can also study the elastic free energy of a confined and deformed chain what should give information complementary to the previous one concerning chain structure elucidated from the frequency of polymer-surface contacts. The free energy A can be calculated according to the formula

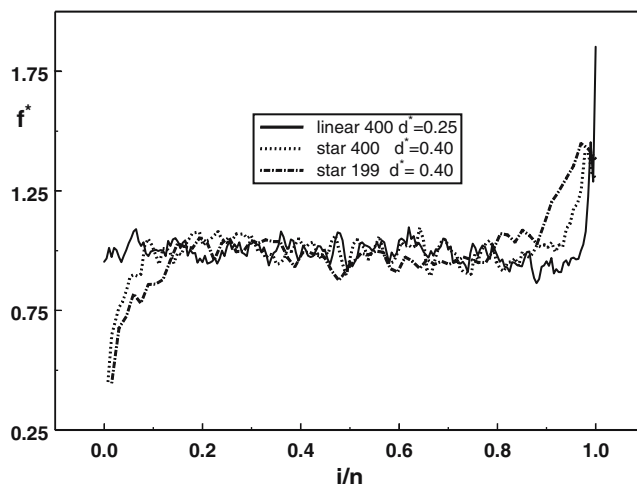


Figure 6. The reduced frequencies of polymer-surface contacts f^* as a function of the bead number i . The chain architectures and the chain lengths are given in the inset.

$$A = c - k_B T \ln[w(\mathbf{R})], \quad (3)$$

where $w(\mathbf{R})$ is the chain end-to-end vector distribution, k_B is the Boltzmann's constant, T the temperature and c is a constant including the free energy of 'free' unconfined chain [8]. In the case of confined and squeezed chains it is interesting to study the differences in free energy of deformation in directions A_{\parallel} parallel and A_{\perp} perpendicular to the confining surfaces. Therefore, we calculated the z and xy component to the distribution of the \mathbf{R} vector $w(\mathbf{R}_z)$ and $w(\mathbf{R}_{xy})$. It was shown [9] that this kind of distribution can be approximated by the Gaussian function and then, the free energy was calculated according to the equation (3). The elastic free energy of 'free' (unconfined) chain was assumed as a state of reference and thus the parameter $c = 0$. Figures 7(a,b) present the both contributions to the elastic free energy in the direction perpendicular (z) and parallel (x) to the surfaces for linear and star-branched chains respectively. One can observe that in general the behavior of all curves is qualitatively similar for all confinements and both chain architectures. The basic differences exist between both components of the free energy, A_{\parallel} parallel and A_{\perp} . The parallel component is only slightly dependant on the size d , especially for linear chains: for the latter case almost fivefold increase of d (from 5 to 24) causes changes of A_{\parallel} on the level of few percents. The perpendicular component is surprisingly almost twice larger for the linear chains than that for star-branched systems. This is caused by a apparently shorter linear fragments (consisting of two branches of a total length $2/3N$) than for the case of the linear chain consisting of N beads, in spite the fact that the total number of beads is the same for both architectures.

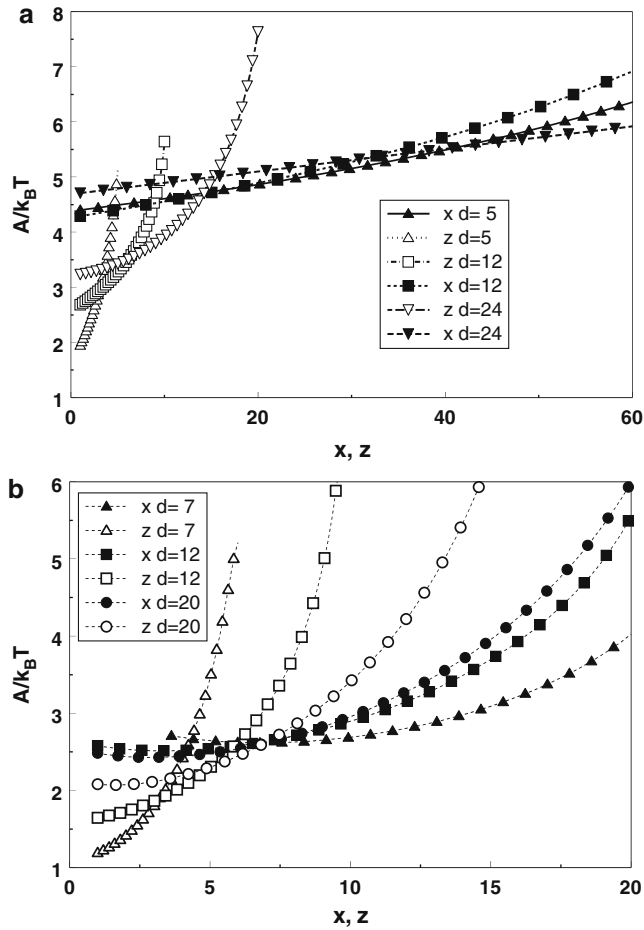


Figure 7. The elastic free energies of chains deformed along the surfaces $A_{||}(x)$ and in the perpendicular direction $A_{\perp}(z)$. The case of the linear chain with $N = 67$ segments, (a) and star-branched chain with $N = 67$ segments. The distances between surfaces d are given in the insets.

4. Conclusions

The simulations of the star-branched and linear chains in confined space were carried out. Despite of the simplicity of the models used one can draw qualitative and interesting conclusions. The results show some differences between the properties caused by the different architecture. It was shown that the static properties of confined polymer chains depend on the degree of the confinement. The reduced chain's as a function of the compression ratio defined as the relation of the chain dimension to the size of the slit does not depend on the chain architecture. The analysis of the interaction between the chains and confining walls enabled one to conclude the presence of a hard core in a vicinity of a

branching point for star-branched chains. It was found that there exist differences in the susceptibility of the systems under consideration on the deformation by the confinement. The star-branched chains were less affected by the confinement than their linear counterparts having the same mass.

References

- [1] R. Eisenriegler, *Polymers Near Surfaces* (World Scientific, Singapore 1993).
- [2] I. Teraoka, *Progr. Polym. Sci.* 21 (1996) 89.
- [3] S. Granick, *Science* 253(1991) 1374.
- [4] Y.-K. Cho, H. Watanabe and S. Granick, *J. Chem. Phys.* 110(1999) 9688.
- [5] A. Halperin and S. Alexander, *Macromolecules* 10(1987) 1146.
- [6] A.E. van Giessen and I. Szleifer, *J. Chem. Phys.* 102(1995) 9069.
- [7] A. Milchev and K. Binder, *Eur. Phys. J. B* 3(1998) 477.
- [8] P. Cifra and T. Bleha, *Macromol. Theory Simul.* 8(1999) 601.
- [9] P. Romiszowski and A. Sikorski, *J. Chem. Phys.* 116(2002) 1731.
- [10] A. Sikorski and P. Romiszowski, *J. Chem. Phys.* 120(2004) 7206.
- [11] A. Sikorski, *Macromol. Theory Simul.* 2(1993) 309.
- [12] M. Daoud and J. P. Cotton, *J. Chem. Phys.* 43(1982) 531.